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Ultrasonic Crystallization of Calcium Carbonate in Presence of Seawater Ions

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HIGHLIGHTS

- Ultrasonic technique was used as a pretreatment method to remove $CaCO_3$.
- The fundamentals of nucleation, growth, form and morphology of $CaCO_3$ were investigated.
- Ultrasound accelerates the nucleation of $CaCO_3$ by 60–85% in induction time.
- Spherical vaterite aggregates constitute to 90% of crystals in most ion systems.
- F^- and Na^+ favor the formation of calcite to a molar fraction of 70%.

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ABSTRACT

Ultrasonic technique was applied to remove the scaling compound $CaCO_3$ as a pretreatment method in desalination process. Supersaturated solution of calcium carbonate was treated with an ultrasonic probe to precipitate $CaCO_3$, followed by filtration to remove the precipitates. The fundamentals of nucleation, growth, crystal form and morphology of $CaCO_3$ in the presence of the major seawater ions and ultrasound were investigated. Naked eye observation on induction time showed that ultrasound accelerates the nucleation by 60–85% though the major seawater ions delay the occurrence of nucleation up to 3 times longer. Continued ultrasound treatment after nucleation accelerates the growth rate by 2–5% only. Metastable vaterite with morphology of spherical aggregates constitutes ~90% of the obtained precipitates in most solution systems except F^- and Na^+, which favors calcite formation. Ultrasound treatment makes the aggregated crystals more fragile and breakable. As a pretreatment method, ultrasound technique not only accelerates the precipitation rate of $CaCO_3$, but also has an effect in inhibiting the crystals growing into compact aggregates.

1. Introduction

Scaling problem is encountered in many industrial water treatment processes. The scaling film in heat exchanger leads to blockage of water channel, increase resistance in heat exchanger and deteriorates the performance of process equipment; scaling film on the surface of membrane causes blockage of membrane pores, imposes limitations to the efficiency of water recovery in desalination process [1] and is costing industries billions of dollars annually [2]. Among the scaling components, calcium carbonate is one of the most common scale in scaling layer [3,4].

The techniques for scale control can be divided into three main categories: those that affect solubility, those that alter the growth mechanism of crystals, and those that change the potential of a surface to foul. Although various techniques have been used to reduce calcium carbonate scale [5–7], they usually cause some other problems, such as high cost of added chemicals, process water being polluted by additives, waste of water by purging, and low efficiency. There are also a number of alternative non-chemical treatment options available, such as magnetic, electronic and electrolytic device treatment [8–11]. Among these non-chemical methods, a more economical and green method, ultrasonic treatment received much attention due to its enhancement effect in crystallization processes [12–17].

When ultrasonic is applied to liquid medium, it exerts alternative cycles of compression and rarefaction within a liquid, creating bubbles during rarefaction stage. The bubbles survive repeated cycles of compression, rarefaction until a critical size is reached, and collapse occurs, initiating a well-known phenomenon of cavitation. Through cavitation, i.e., rapid formation, growth, and violent collapse of bubbles, power ultrasound promotes and enhances chemical and physical changes. The mechanisms of single-bubble and multi-bubble cavitation show

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that a collapsing bubble behaves as a particular micro reactor where high-energy species (ions and radicals) and excited states may be involved in the reaction outcome. Cavity collapse near a liquid–solid interface generates effects of destruction of boundary layers and mass and heat transfer improvements. Ultrasonic method is sought as an effective way of achieving faster and uniform primary nucleation, relatively easy nucleation of particles at lower supersaturation levels, reduction of agglomeration, etc. [18].

Sonication has been applied to the precipitation of calcium carbonate in aqueous system. Nishida et al. has shown that the physical effect of mixing, which depends on horn immersion depth, intensity and diameter of horn tip, has a proportional effect on deposition rate, while the chemical effect was not found to affect the deposition rate, nor does cavitation [13]. Dalas reported a retardation effect in growth rate of calcium carbonate by 62% at ultrasonic intensity of 80 W/mL [12]. Conversely, Boels et al. found that the volumetric crystal growth rate of calcite in seeded sonocrystallization was enhanced by 46% at 42.15 Hz and 17 W/L [15]. Wagterveld et al. also found that the occasion of ultrasound application has a different effect on the nucleation of calcium carbonate [1]. Nasser et al. further monitored the crystallization kinetics of calcium carbonate in situ by using Focused beam reflectance measurement (FBRM), and observed that the ultrasound causes a higher nucleation rate and number counts, but slower growth rate and reduced crystal size mainly in a class of 1–5 μm [16]. Price's work also supported the results above, and further suggested that smaller particle size precipitated through cavitation effect when collapse is more intense and produce stronger jets at lower temperature [19]. In respect of form, calcite is generally enhanced by ultrasonic. Content of calcite after ultrasonic treatment was found having a proportional relationship with ultrasound intensity (between 0 and 20 W/cm^2), while vaterite form having a reverse proportional relationship, and calcite was the main form when sonication time is longer than 30 min [19]. Berdonosov et al. found that the transition of metastable vaterite to calcite can be enhanced by ultrasonic treatment [2].

Findings on the ion effect in the calcium carbonate crystallization are mostly focused on Mg^{2+} and SO_4^{2-}, which have obvious effect in hindering the growth of calcium carbonate crystals. The presence of Mg^{2+} and SO_4^{2-} ions in the solution increases the nucleation time and decreases the growth rate [20–23], mostly promotes the aragonite form [20,23,24], and has the possibility to incorporate into the lattice of calcium carbonate crystals depend on the concentration, temperature and growth rate [20,25,26]. However, the effects of other ion species on the crystallization of calcium carbonate are incompletely investigated. $Sr^{2+}$was found to promote the aragonite formation [26],and does not affect the shape, size or lattice of aragonite crystals [27]. K^+ stabilizes the crystalline [hk0] faces on the [104] rhombohedra calcite crystals. F^- inhibits the adsorption of Mg^{2+} on calcite surface [26].

Application of ultrasound is expected to accelerate the precipitation of calcium carbonate in concentrated seawater system and may be useful as a pretreatment technique to avoid scaling in the following desalination steps, e.g., MSF (Multistage Flash) or RO (Reverse Osmosis). However, none of the literatures has concerns with the effect of the ultrasonic treatment and seawater ions (K^+, Mg^{2+}, Sr^{2+}, SO_4^{2-}, F^-, Br^-, Na^+, Cl^-) on the crystallization of calcium carbonate systematically. In this study, ultrasound was applied in solutions with single seawater ion specie respectively to accelerate the precipitation of calcium carbonate. The nucleation, growth rate, form transformation and morphology characteristics of calcium carbonate during the sonocrystallization process were systematically investigated in this paper.

2. Experimental

Only analytical grade reagents, high quality water and grade A glassware were used throughout the experiments. Reaction solutions of $CaCl_2$ (50.00 mmol/L) and $NaHCO_3$ (13.40 mmol/L) were prepared using deionized water. The major ions in seawater were dissolved singularly in the above solution before reaction (Table 1) and then were investigated separately on the effect of calcium carbonate ultrasonic crystallization. The pH value of $NaHCO_3$ solution was adjusted to 8.70. All solutions were filtrated with 0.15 μm membrane to remove any particles before reaction.

The experiments were carried out using the setup as shown in Fig. 1. Ultrasound was generated by an ultrasonic homogenizer on which a horn with a diameter of 6 mm is mounted. The power and intervals of sonication treatment can be set with a controller. Frequency of 20 KHz and 90% of the maximum power (1045 W) were used during the experiment. Reactions were taken place inside a jacket crystallizer of 57 mm in diameter and 100 mm in height. The horn was immersed in the center of the bulk solution both horizontally and vertically to make sure that the radiation is homogeneous throughout the whole vessel [13]. 200 mL supersaturated solution of calcium carbonate were prepared by mixing 100 mL $CaCl_2$ solution and 100 mL $NaHCO_3$ solution under stirring at 20 °C. Ultrasound was initiated right after the mixing was completed, and then was kept for 30 min after nucleation was observed. Induction time was recorded with a stopwatch at the moment of the first white crystal was observed by naked eyes. During the experiments, samples of slurry were collected and filtered through a 0.15 μm syringe filter. The solid samples were washed with distilled water and dried in vacuum at 80 °C. Method of EDTA chelatometric titration was used for analysis of concentration of calcium ion. The crystal morphology and element analysis were examined with SEM (Hitachi, S4800) and EDS (Ametek Octane Pro) respectively. Solid form characterization was performed with X-Ray (Bruker, D8 Focus).

The molar fraction (%) of calcium carbonate polymorphs was determined using the intensity of the [221] plane of aragonite, the [104] plane of calcite and the [110] plane of vaterite in the XRD pattern [28].

For mixture composed of calcite and aragonite:

$$X_A = 3.157 \times I_A^{221} / \left(I_C^{104} + 3.157 \times I_A^{221}\right) \quad (1)$$

$$X_C = 1 - X_A. \quad (2)$$

For mixture composed of vaterite and calcite:

$$X_V = 7.691 \times I_V^{110} / \left(I_C^{104} + 7.691 \times I_V^{110}\right) \quad (3)$$

$$X_C = 1 - X_V. \quad (4)$$

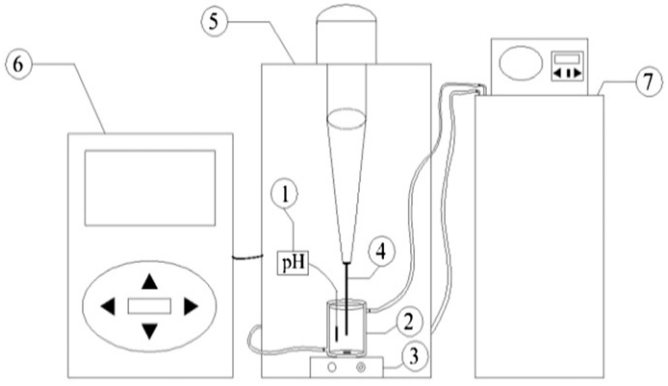

Fig. 1. Experimental setup of sonocrystallization: ① pH meter, ② jacket crystallizer, ③ magnetic stirrer, ④ probe, ⑤ soundproof box, ⑥ ultrasonic controller and ⑦ water bath.